

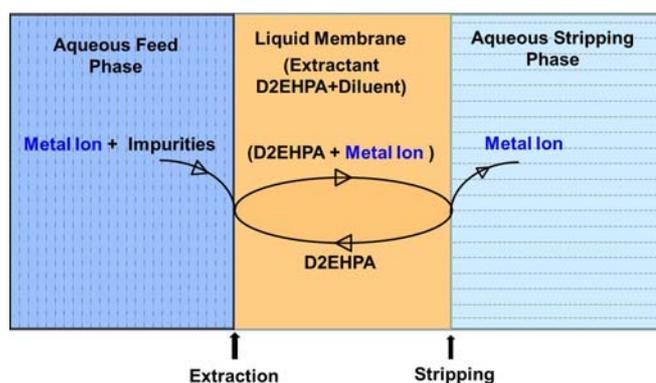
USE OF D2EHPA-MEDIATED LIQUID MEMBRANES FOR HEAVY METAL IONS SEPARATION: A REVIEW

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The removal and recovery of heavy metal ions by various types of liquid membranes (LMs), coupled with the commercial extractant di-2-ethylhexyl phosphoric acid (D2EHPA) as carrier, have been extensively studied by many researchers. In this paper, the D2EHPA-mediated LM systems used for transport of heavy metal ions are classified, briefly summarized, and reviewed. The effects of the system chemical compositions and the LM configurations on the separation selectivity and the transport efficiency are evaluated. It seems that depending on the way of choosing the chemical composition of the D2EHPA system, the formed LMs can separate selectively one or a mixture of heavy metal ions. Practically, D2EHPA-mediated LMs can be applied in a laboratory-scale as separation and preconcentration step for a heavy metal ion over the detection limits of routine analytical instruments. For large-scale applications on the removal and recovery of the heavy metal ions from waste water or industrial effluents, further modifications and improvements to the existing LM configurations should be developed in order to surmount certain problems such as slow transport rate or reduced stability of some LMs.



INTRODUCTION

Efficient separation and recovery of heavy metal ions from wastewaters and industrial streams as well as from raw materials is gaining more and more importance due to the reduction of their harmful impacts on health and environment¹⁻³ and to the economic benefits of recovered metals.^{4,5} Heavy metal ions are often introduced into the processing effluents resulting from many hydrometallurgical and chemical industries such as metal plating, electroplating, and production of batteries, stabilizers, pigments, pesticides, fertilizers, and cement.⁶ Conventional separation methods devoted for treatment

of wastewaters containing heavy metals often include solvent extraction,⁷ precipitation,⁸ adsorption,⁹ ion exchange.¹⁰

In the last 30 years, liquid membrane (LM) as separation method has been received important attention by researchers because this process has several advantages over conventional separation methods such as ease of operation, use of minimal amount of solvent, low energy consumption, low operation costs, continuous operation, and combination of both the extraction and stripping steps in a single unit operation, etc.¹¹⁻¹⁴ Moreover, there is another interesting advantage of LM method is that the overall mass transfer process is

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governed by kinetic rather than equilibrium conditions.¹⁵

The LMs can efficiently employ the common chemical extractants such as organo phosphorus compounds,¹⁶⁻¹⁹ amine extractants,^{20,21} macrocyclic ligands.²²⁻²⁴ The extractant used in LMs plays a role of a carrier that takes the metal ion from feed phase and releases it into stripping phase; so the process is called carrier-mediated LM transport. Among these extractants, Di-(2-ethylhexyl) phosphoric acid (D2EHPA) has been widely used for recovery of a variety of heavy metals from acidic solutions in hydrometallurgical processes.²⁵ It has stable chemical composition, good kinetics of extraction, good loading and stripping characteristics, low solubility in the aqueous phase and is available in commercial quantities. However, the use of D2EHPA in solvent extraction suffers sometimes from tendencies of third phase and crud formation at interface as well as some losses of D2EHPA amount from organic phase. These drawbacks may be eliminated using LMs.²⁶

The survey of literature indicates that significant number of research works has investigated the use of D2EHPA as a carrier through various LM configurations for separation of the heavy metals. The aims of these works were to develop LM systems owing both higher efficiency and selectivity towards heavy metal ions, to test the feasibility of some developed LM configurations for transport processes, and to find useful practical applications in metal separation processes.²⁷ Some carrier-mediated LM systems have been already found an application in the field of the analytical chemistry as an answer for the analysis problems of trace metals.²⁸ In fact, the LMs may play a promising role as feasible tool for preconcentration of low trace metals in natural waters,²⁹ *i.e.* in the concentration ranged from from 10^{-7} to 10^{-12} mol/L.

The current paper aims to review most of research works accomplished about using D2EHPA-mediated LM systems for heavy metal ion separations. The effects of the system chemical compositions and the LM configurations on the separation selectivity and the transport efficiency are briefly summarized. The collected information and results are critically reviewed. General remarks and suggestions are given to find useful applications for D2EHPA-mediated LMs in analytical laboratories or separation processes.

CONFIGURATIONS OF LIQUID MEMBRANES

A variety of types of LMs exists; *i.e.*, bulk liquid membrane (BLM), emulsion liquid membrane (ELM), supported liquid membrane (SLM), and polymer inclusion membranes (PIM).^{30,31}

BLMs usually consist of aqueous feed and stripping phases separated by a bulk organic membrane phase.³² The most used configurations of BLMs in the laboratories are U-tube (Fig. 1a) and coaxial cylinders-type (Fig. 1b).^{33,34} BLMs have used so far for basic studies of transport since they provide low interfacial area and poor mixing of the three phases.³⁵

In supported liquid membranes, a microporous membrane is impregnated with an organic solvent and then sandwiched between an aqueous feed and strip solution.³⁶ The microporous membrane for the SLM can be flat-sheet (Fig. 2a) or hollow fibers (HFSLM) (Fig. 2b). In the configuration of HFSLM the fiber wall is impregnated with the liquid membrane phase, the feed solution flows through the lumen of fibers, and the strip solution flows through the shell side of the fibers or vice versa. The hollow fiber geometry is particularly advantageous because its interfacial area is much higher than that of flat-sheet SLM.³⁴

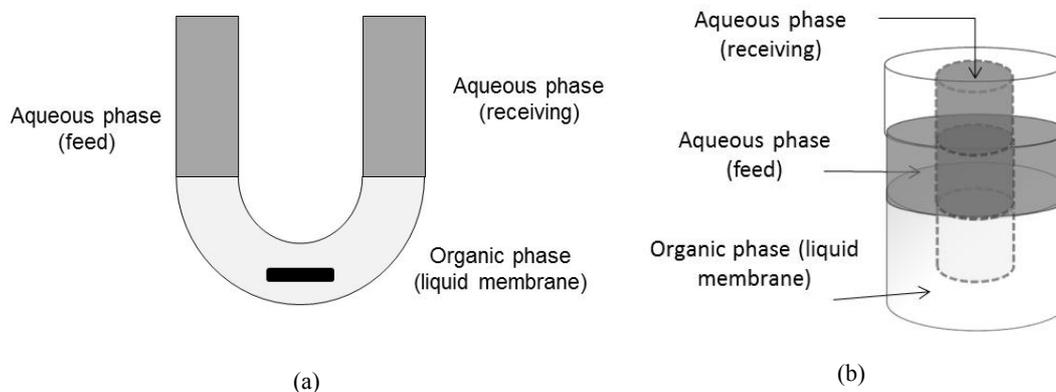


Fig. 1 – Schematic representations for BLMs' configurations: a) U-shaped tube, b) coaxial cylinders.³⁴

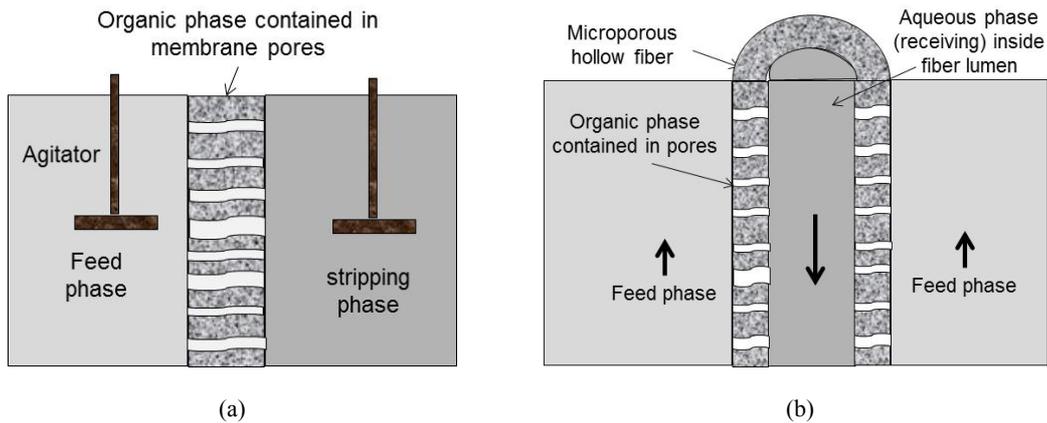


Fig. 2 – A schematic representation of the SLM configurations: a) scheme of flat SLM³², b) Scheme of HFSLM.^{36,38}

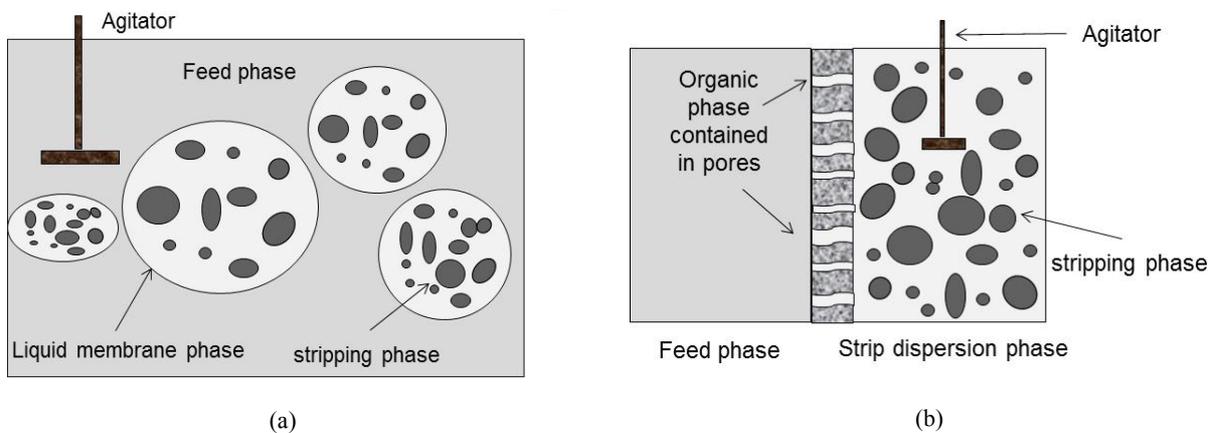


Fig. 3 – A schematic representation of ELM configurations: a) ELM,³² b) Combined SLM/strip dispersion process.³⁸

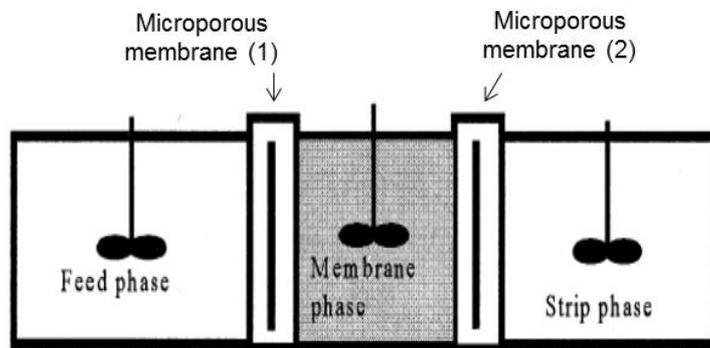


Fig. 4 – Multimembrane hybrid system (MHS). Two membranes are employed as phase separators.³²

ELMs (Fig. 3a) are prepared by dispersing an inner aqueous receiving phase in an immiscible organic liquid membrane phase to form a stable emulsion by the help of surfactants.³⁷ This emulsion is then dispersed by mechanical agitation into an aqueous feed phase containing the metal to be extracted. The transport of the solute(s) takes place from the continuous outer feed phase through the LM phase to the inner stripping phase. This configuration has the advantage of high interfacial area between the phases.³³

Based on a combination of SLMs and ELMs a new configuration (Fig. 3b) has been developed and denoted supported liquid membrane/strip dispersion.^{38,39} This configuration does not use a high active surfactant and demulsification device, but rather high-shear mixing between the organic and strip phases, and then provides an extra mass transfer surface area.

There is another novel type of liquid membrane, called “multimembrane hybrid system (MHS)”, composed of two sets of porous solid membranes

separating the liquid membrane from the feed and stripping solutions.³² The transport process takes place by pertraction through liquid membrane.

Polymer inclusion membranes (PIMs) are composed of a thin, stable polymer containing an ion selective carrier and a membrane plasticizer.^{33,40,41}

The resulting membrane is used to separate source and receiving phases.

SEPARATION OF HEAVY METAL IONS AS A SINGLE CATION IN FEED PHASE

D2EHPA-mediated LMs have been applied in research works to separate a heavy metal cation as a single ion in feed solutions.

Cadmium

A BLM containing D2EHPA was used in kerosene for separation and preconcentration of cadmium in samples of natural and sea waters prior to the spectrometric determination of cadmium.⁴² This work indicated that other cations such as calcium and magnesium were co-transported through the membrane and decreased the effectiveness of cadmium permeation. This problem was overcome by masking calcium and magnesium with the addition of citric acid. By working under optimum equilibrium and hydrodynamic conditions, a cadmium ion transport percentage of 100% was obtained for both synthetic and real seawater. The method was successfully applied to the determination of cadmium in real seawater. The authors reported that their new method based on LMs can offer advantages such as simplicity, lower time needed for sample pre-treatment, and lower sample manipulation which is very important in trace analysis to prevent sample contamination.

The transport of cadmium ions from an aqueous solution by an ELM system containing D2EHPA was studied.⁴³ The parameters of the proposed system were experimentally optimized, then studied in order to understand the various resistances to mass transfer in the system and identify the rate limiting steps. Under the optimal conditions, the initial cadmium ion concentrations ranging from 20 to 1000 ppm have reached a very low concentration (less than 0.5 ppm) in the outer aqueous phase. Another result of this study is that the main resistance to mass transfer may lie at the outer oil–water interface, while varying the inner

oil–water interfacial area does not affect the overall rate of mass transfer.

A HFSLM configuration was studied for transport of Cd(II) ions.⁴⁴ The study focused on the effect of aqueous solution velocities and D2EHPA carrier concentrations on mass transfer of Cd(II) ions. It was found that the cadmium ion permeability increased when increasing the velocities of feed and stripping phases. This result confirms that the rate limiting steps were the diffusion of ions through both aqueous films along the feed and the stripping sides of the membrane. Under the applied operation conditions, an initial cadmium ion concentration of (0.012±0.003) mg/L in water is reduced around 40%.

He *et al.*³⁹ used the configuration of SLM/strip dispersion for the simultaneous removal and recovery of Cd(II) and CN⁻ from simulated electroplating rinse wastewater by D2EHPA and trialkyl-phosphine oxide (TRPO) carriers. The authors attempted to remove these two kinds of toxic pollutant in wastewater generated on a large scale in hydrometallurgy, electroplating, and other industries. The run of the ions transport experience during 6 h and at pH 5.5 in feed phase the content of CN⁻ or Cd(II) reduced to 0.05 and 0.02 mg/L, respectively. The recovery percentage of both cadmium and cyanide in stripping solution was more than 99%.

Lead

Benomar and coworkers have developed and optimized two LM systems, a BLM⁴⁵ and a spiral flowing SLM,⁴⁶ to be separation and preconcentration steps of lead ions by D2EHPA as an active carrier from seawater samples into the acidic phase. A determination of lead concentration in receiving phase is subsequently measured by inductively coupled plasma-mass spectrometry (ICP-MS). Under the optimized conditions, an extraction yield was (93.8±0.1)% in the two configurations. The preconcentration factor obtained in the case of the SLM system (14.2) was better than that obtained by the BLM (4.7). This can be explained by the use of smaller volumes of organic and stripping phases in the SLM configuration. The interference of other ions with Pb(II) ions did not be discussed in this study. Besides that, SLM filters were analyzed by electron microscopy after each period of 2 h and several microparticles and other deposits in form of a thin layer were observed in the polymeric

support. These modifications cause reduction in live age of SLM. However, the proposed LM systems have allowed both successful lead ion selective separation and accurate determination in real and saline samples at environmental concentration levels.

The use of an ELM configuration for removal of lead (II) from aqueous solution by D2EHPA was extensively studied.⁴⁷ The results demonstrated that both the stability of the emulsion and the removal efficiency increase with the increase of the concentration of sulphuric acid, used as stripping phase, from 0.25M up to 1M; and behind this value the ELM stability decreased. On the other hand, increasing the used surfactant concentration up to 8% v/v improved the emulsion stability but increased both the surfactant film resistance and the viscosity of the organic phase resulting in lowering the mass transfer in the lead removal process. So it concluded that the surfactant concentration must not exceed (4% v/v) to achieve 99% lead removal efficiency.

Shama *et al.*⁴⁸ studied the removal of Pb(II) from contaminated aqueous waste using ELM made up of D2EHPA as an extractant, cyclohexane as a diluent, sulfuric acid as a stripper and Span-80 as a surfactant. An increase of the sulfuric concentration in the internal phase in the range (0.01–0.1M) increases rapidly the stripping efficiency, but further increase (0.1–2M) showed no effect; which is probably due to the low initial Pb(II) concentration used in this study (100 mg/L). On the other hand, it was found that an increase in D2EHPA concentration from 2% up to 6% leads to a high increase in extraction rate as a result of increasing carrier capacity. So, using 10 mL of prepared ELM under optimized conditions can extract about 99% of 100 mg/L of lead from its dilute acetate solution after 10 min.

A HFSLM system containing D2EHPA was studied to separate and strip Pb(II) ions from relatively low-level synthetic solutions of Pb(NO₃)₂ and PbCl₂.⁴⁹ When using several tested types of stripping solutions the order of stripping efficiency for Pb(II) was as follows: HCl > H₂SO₄ > HNO₃ >> distilled water. This attributed to more hydrogen ions by acid stripping solutions (HNO₃, H₂SO₄, HCl) resulting in higher mass transport. In the case of HCl, hydrogen ions react with lead and D2EHPA complexes formed in organic phase to produce PbCl₂. With excess HCl concentration, PbCl₂ carry on converting to undissociated PbCl₄²⁻, which could not react with the D2EHPA extractant. As a result, compared to

HNO₃ and H₂SO₄, higher amount of Pb²⁺ (approximately 96–97%) in the stripping phase was observed by using HCl.

Zinc

The effect of D2EHPA concentration variation on the zinc transport through a SLM was studied.⁵⁰ The zinc ions were present in aqueous perchlorate media whose concentration was 1.0 M. The results revealed that the use of very high D2EHPA concentration was not recommendable because it might result in an increase of LM viscosity and consequently in decrease of diffusivity and permeability of the complex species.

He and co-workers have used a combined SLM/strip dispersion system containing D2EHPA in kerosene as the carrier for study of transport and separation of Zn(II).³⁸ The experiments demonstrated that the transport of Zn(II) ions is coupled by the counter-flow of H⁺, and zinc(II) ions can be quickly separated from Cu(II) ions at the optimum value of pH (2.0–2.5). The recovery of Zinc(II) in the strip phase was above 99% after maintaining pH 4.34 in the feed solution. The experiments showed that the uptake of carriers out of the membrane phase into the feed phase increases with rising pH in the aqueous feed solution due to the increase of the solubility of D2EHPA in the feed solution.

The strip dispersion system taking place within hollow-fiber SLM was used for transport zinc ions by D2EHPA.⁵¹ When studying the effect of carrier concentration, a noticeable increase from 78 to 99% in zinc extraction was observed with an increase in the carrier concentration from 2% to 6%. On the other hand, the overall mass-transfer coefficient increases from $12 \times 10^{-6} \text{ m}\cdot\text{s}^{-1}$ at 2% D2EHPA to $28 \times 10^{-6} \text{ m}\cdot\text{s}^{-1}$ at 8% D2EHPA. This means that this process is chemically controlled. Furthermore, when studying the hydrodynamic conditions, the obtained results revealed that the diffusion processes in aqueous feed phase and the membrane phase had the same importance as the chemical process.

Cobalt

The effect of some operating variables on the kinetics of cobalt(II) transport across a BLM containing D2EHPA was studied.⁵² It has been found that cobalt transport increased with both stirring of the receiving phase and its acidity, while

the presence of emulsifier reduced this transport, particularly at the membrane/receiving phase interface. Moreover, the mean cobalt transport rate was practically independent of the membrane/feed solution interfacial area, while this rate substantially increased with the initial cobalt concentration in the feed solution.

The effect of various emulsifiers (Span 80, polyamine, ECA 4360-III, and Paranox 100) and surface-active substances on pertraction of Co(II) in through BLM and ELM systems containing D2EHPA were investigated.⁵³ If no emulsifier was present in a BLM system, initial flux of Co(II) cations through the feed-membrane solutions interface was more six times higher than flux through the stripping-membrane solutions interface, thus the stripping process was much slower than the extraction process. All tested emulsifiers decelerated initial fluxes of Co(II) through the two interfaces. Fluxes were decreased much more in the presence of polyamine-based emulsifiers compared to Span 80, due to more condensed adsorption films created by polyamines at the interfaces. On the other hand, the authors reported that an addition of alkylphenol sulphides (AFS-II) as surface-active substance to the membrane solution containing the emulsifier (ECA 4360-III) almost doubled cobalt pertraction through the membrane-receiving phases interface. Experiments with the ELM system in its turns confirmed differences in pertraction found in the BLM.

The effect of D2EHPA and stripping solution H₂SO₄ on the transport kinetic of cobalt(II) ions through BLM was studied.⁵⁴ It was found that an increase of either the carrier or the counter ion concentration (H₂SO₄) leads to an important increase of cobalt maximum flux through the BLM. The cobalt(II) recovery percentage was almost 95% after 24h of operation.

Asharf Chaudry *et al.*⁵⁵ studied the effect of the concentrations of D2EHPA and the stripping solution HCl on the transport of Co(II) through SLM using CCl₄ as diluent. Maximum flux and permeability values were obtained at a 0.87 M carrier concentration in the membrane and at 1 M HCl concentration in the stripping phase. By increasing carrier concentration from 0.87 to 2.03 M, the distribution coefficient of Co(II) ions into organic phase has been found to increase from 1.8 to 30, while the flux determined decreased from 1.25×10^{-5} to 0.95×10^{-5} mol.m⁻². The decrease in the matter flux values at carrier concentrations above 0.87 M was explained by the increase in viscosity of the LM phase. It can be noticed that the cobalt

recovery percentage was low (40%) in this CCl₄-based membrane system compared with other systems using kerosene as diluent for D2EHPA where 90% to 95% of the metal were recovered.^{52,54}

Nickel

Bayen *et al.*⁵⁶ used SLM containing a mixture of D2EHPA and 1,10-didecyl-1,10-diaza-18-crown-6 ether for the separation and preconcentration of very low traces of free nickel ions Ni(II) in aqueous samples. The work profoundly aimed at studying nickel speciation in aqueous samples. In this work, the composition of the organic phase was studied to maximize the Ni flux (thus the sensitivity of the system) over a wide Ni(II) concentration range (5×10^{-8} M to 0.1 M) in order to verify its ability to determine free Ni(II) in the presence of Ni complexes. The used SLM was shown to be a reliable tool to measure free nickel concentrations Ni(II) down to 10^{-7} M in the presence of Ni complexes.

Copper

A D2EHPA-mediated BLM system was used for preconcentration of the copper ions in aqueous samples prior to his determination by flame atomic absorption spectroscopy.⁵⁷ The optimized preconcentration system transported 87.0% of Cu(II) ions present in real samples, and the copper preconcentration factor was (4.30).

The extractability of D2EHPA was compared with other well-known extractants, CYANEX 272 (bis-2,2,4- trimethyl pentyl phosphinic acid) and LIX 984N (mixture of 5-nonylsalicylaldoxime and 2-hydroxy-5-nonylacetophenoneoxime), as carrier for transport of copper across BLM.⁵⁸ The results were that the highest maximum flux and the best Cu(II) ion transport were obtained using LIX 984N as a carrier (higher than 80%), whereas the lowest maximum flux and the worst copper transport is obtained using D2EHPA (lower than 70%).

Chang *et al.*⁵⁹ studied the optimization of operating parameters of Cu(II) ions removal and recovery from aqueous solutions by D2EHPA contained in soybean oil-based BLM. The soybean oil is used as greener solvent instead of petroleum-based organic solvents. The obtained experimental data indicated that the removal and recovery process was improved greatly by stirring either the feed, membrane, or all phases. Furthermore, the recovery process was improved when applying a

larger stripping/membrane interfacial area available for the transport of Cu(II) from membrane into stripping phases. When applying the optimal operation conditions, the experimental recovery percentage of Cu(II) was (98.56%).

The D2EHPA-mediated BLM was used for separation of Cu(II) ions from ammoniacal leaching solutions.⁶⁰ In ammoniacal feed solution the predominant metallic specie of copper was the complex $(\text{Cu}(\text{NH}_3)_4^{2+})$. This copper species is extracted by D2EHPA. It was found that copper transport was greatly affected by stirring speed and the pH of both aqueous phases, while temperature influenced weakly the copper transport. The extraction of copper from ammoniacal solution (feed phase) at pH 10 was very fast reaching 98% after just 1 h while only 2% of copper remained into the membrane at the end of the operation. At pH values of 11 and 12 the receiving phases stripped lower amounts of copper than in case of pH 10. The authors speculated that a stable complex was formed between the carrier and $\text{Cu}(\text{NH}_3)_4^{2+}$ that was difficult to dissociate at the membrane/ receiving interface leading to decrease the efficiency of copper transport from the membrane.

SEPARATION OF MIXTURE COMPONENTS OF HEAVY METALS IN FEED PHASE

The ability of BLM containing D2EHPA in simultaneous transport of mixture components of copper, nickel and zinc metal ions was studied.⁶¹ This study revealed LMs could be applied as the novel techniques of mixture component separation. In fact, maximum extraction of 98.8% of zinc, 95.8% of copper and 95.0% of nickel metal ion was achieved at the optimum conditions. Also, it was found that increasing the pH difference resulted in a decrease in final source phase concentration.

The removal of Cd(II) and Zn(II) was tested through SLM using D2EHPA and mono-(2-ethylhexyl) ester of phosphoric acid (M2EHPA) as carriers.⁶² The results showed that, under optimum conditions, a mixture of D2EHPA and M2EHPA is a more proper carrier for the pertraction of Cd(II) and Zn(II) ions than D2EHPA. In the experiments at feed phase pH 0.5, the recovery percentage was 90% and 60% for Cd(II) and Zn(II), respectively. Also, the pertraction performance for single ion solutions in the feed phase was higher than that for the equimolar

solution of Cd(II) and Zn(II) due to the competitiveness between these metal ions.

Mendiguchia *et al.*⁶³ have developed a BLM system and applied it to the simultaneous separation and preconcentration of up to seven heavy metals (copper, zinc, lead, cadmium, aluminium, manganese, and nickel) in seawater. The LM system achieved preconcentration yields varied in the following order (at feed phase pH=5.5): Cu (77.77%) > Zn (74.06%) > Pb (57.88%) > Mn (56.79%) > Ni (51.93%) > Al (44.97%) > Cd (44.11%). The proposed system was applied to the preconcentration of four real seawater samples before their quantification by inductively coupled plasma–mass spectrometry (ICP–MS).

The selectivity of D2EHPA for zinc transport from multicomponent mixture (zinc, iron, calcium, and magnesium) as well as the transport modeling were studied through SLM.⁶⁴ It was observed that Ca(II) and Mg(II) ions were not transported at the pH of the feed phase studied (pH = 2.5), and Fe(II) ions were co-transported partially with zinc ions. A transport rate model was presented considering zinc diffusion to, from and through the membrane as the slow steps. It was found that mass transfer coefficients increased with an increase in the flow rate of feed and stripping phases. Also, an increase in the concentration of hydrogen ions of the stripping phase increased the zinc ion transport yield.

A selective transport of zinc(II) from cobalt(II) sulphate solutions using a SLM impregnated with D2EHPA extractant have been performed.⁶⁵ The studied SLM showed a good efficiency for zinc transport. Under the established optimal conditions (at feed phase pH=3) for the separation of both metals, the percentage extraction of zinc in the receiving phase is equal to 93%, while that of cobalt is less than 6%. Nevertheless, the authors reported that the efficiency of the separation process could be improved by using more effective membrane unit, *i.e.* hollow fiber modules. Moreover, the membrane lifetime was evaluated and stable zinc transport was observed up to the sixth continuous use of the same membrane. Once the zinc transport was suppressed, regeneration of the membrane is achieved by re-impregnating the support membrane, and then the zinc transport ability was recovered.

Swain *et al.*¹⁶ studied the effect of different anions on separation of cadmium and zinc by SLM using D2EHPA. These metal ions are often associated with different anions such as Cl^- , NO_3^- , SO_4^{2-} , CH_3COO^- , SCN^- , and ClO_3^- . The fluxes and separation factors depends upon various physical and

chemical properties, i.e. the size, charge, polarizability, shielding hard-sphere diameter and nucleophilicity of anions. It was observed that, the highest zinc flux and the highest separation factor were obtained when there were no additional electrolyte salts. In the presence of 10 mol/m^3 of NaCl, NaNO₃, Na₂SO₄, CH₃COONa, NaSCN and NaClO₃ of added salt solutions in feed, the zinc flux decreased and its values are within the following range $(8.4-3) \times 10^{-6} \text{ mol.m}^{-2}\text{s}^{-1}$, but cadmium flux remained constant at $0.125 \times 10^{-6} \text{ mol.m}^{-2}\text{s}^{-1}$. The highest zinc separation factor with different salts solution follows the following descending order NaCl (39.04) > NaSCN (30.61) > CH₃COONa (27.89) > NaNO₃ (23.55) > Na₂SO₄ (20.02) > NaClO₃ (13.94). At pH 2.25 the co-permeation of cadmium with zinc was negligible, so the highest separation factor was obtained at this pH.

A multimembrane hybrid system (MHS) coupled with D2EHPA was developed for improving the performance and the efficiency of zinc ions separation processes from multicomponent mixtures (Zn, Ca, Cu, Mg, K, and Na).⁶⁶ The obtained results indicated that the fluxes of Zn(II) and Ca(II) were dominant attaining >90% of the overall flux. However, because of known affinity of D2EHPA towards competing calcium cations, the fractional fluxes of Zn(II) are only 55.2% of the overall flux. The results concerning separation effects indicated the following selectivity order for MHS: Zn > Ca > Cu >> Mg > K, Na. Based on this selectivity order, and the high permeability coefficients, the authors reported this system can be applied for the recovery of Zn(II) from multicomponent mixtures on condition that the feed does not contain calcium cations. It is noteworthy that there is more recent study⁶⁷ in which the zinc ions were transported as single ion through D2EHPA-mediated MHS and the transport yield was more than 99%.

A polymer inclusion membrane (PIM) containing D2EHPA for selective removal of manganese(II) and nickel(II) from acidic chloride solution was studied.⁶⁸ The obtained results indicated that the transport rate of Mn(II) and Ni(II) increased with increasing of the used membrane plasticizer concentration. Under the optimal applied conditions the selectivity coefficient of Mn/Ni was equal to (2.76).

DISCUSSION AND GENERAL REMARKS

The previous literature reveals that many research works have been devoted to the use the

commercial extractant D2EHPA as carrier in the different LM types for separation of heavy metal ions. These works led to prove that the D2EHPA-mediated LMs are reliable methods for removal and recovery of heavy metal ions such as copper, zinc, lead, cobalt, nickel, and cadmium. Depending on the way of choosing a chemical composition of the two aqueous feed and receiving phases as well as the LM phase, the D2EHPA-mediated LMs can separate selectively one or a mixture of heavy metal ions.

The performed research works have been conducted for several goals. A part of research was mostly focalized on the establishment of the optimal chemical composition so that the overall system selectivity was as higher towards a target heavy cation(s) as possible. Upon the optimization of chemical composition conditions, optimal hydrodynamic conditions related to the used LM configuration were subsequently established in order to best accelerate the metal ion transport through LM. The most examined chemical factors affecting the selectivity and the transport yield are metal cation type, diluent, potential synergetic effect of another carrier, types of counter-ions and co-ions present with a target cation(s) in feed phase,¹⁶ surfactant type,^{47,53} and stripping agent type,⁴⁹ as well as concentrations of all these chemical components involved. The effects of these factors on the transport and separation of heavy metal ions by D2EHPA-mediated LMs can be discussed as follows:

- Metal ion transport increases with a higher acidity of the receiving phase⁵² and with a lower concentration of H⁺ ions in the feed solution.⁶⁹ This tendency is due to the acidic extractant nature of D2EHPA which is cation exchanger. Therefore, D2EHPA-mediated LM systems can be applied for heavy metal cation separation from weak acidic aqueous feed phases at which pH can be ranged from 2 to 6 regardless of the medium nature (sulfates, nitrates, or chlorides). Furthermore, the choice of a pH value within this range of the feed phase containing several heavy metal ions plays an important selective role in transporting singly or simultaneously heavy metal ions by D2EHPA-mediated LM systems. Table 1 showed some collected data taken from the previously cited literature about the effect of the pH of the feed phase on the selectivity of D2EHPA-mediated LM systems. It is observed that the pH influenced clearly the resulting selectivity.

Table 1

The effect of the feed phase pH on the selectivity of D2EHPA-mediated LM systems towards heavy metal ions when present simultaneously

Used LM configuration and its reference	Mixture of heavy metal ions in the feed phase	pH	Selectivity*
(SLM) ¹⁶	Zn(II), Cd(II)	2.25	(Zn/Cd) = 39
(PIM) ⁶⁸	Mn(II), Ni(II)	2.76	(Mn/Ni) = 2.76
(MHS) ⁶⁶	Zn(II), Ca(II), Mg(II), Cu(II), Na(I), K(I)	3	Zn (55%) > Ca (37%) > Cu (6.44%) >> Mg (0.06%) > Na (0.04%) > K (0.01%)
(SLM) ⁶⁵	Zn(II), Co(II)	3	Zn(II) = 93%, Co(II) < 6%
(BLM) ⁶³	Cu(II); Zn(II); Pb(II); Mn(II); Ni(II); Al(II); Cd(II)	5.5	Cu (77%) > Zn (74%) > Pb (57%) > Mn (56%) > Ni (51%) > Al (45%) > Cd (44%).
(BLM) ⁶¹	Cu(II); Ni(II); Zn(II)	6	Zn (98%) > Cu (96%) > Ni (95%)

* Selectivity results are expressed as presented in studied researches: either by recovery percentage of metal ion or by a selectivity factor which is the ratios of two metal ions concentrations in the mixture.

- The pertraction performance for single ion feed solutions was higher than that for the equimolar solution of a mixture of ions due to the competitiveness between these metal ions; as it was seen, for instance, in case of separation of Cd(II) and Zn(II).⁶²

- The presence of additional electrolyte salts with target metal ion in feed phase causes the reduction of both the separation factor and mass flux.¹⁶ These added electrolyte salts differently affect the transport properties of heavy metal ion(s) according to the type of conjugate anions.

- The use of very high D2EHPA concentration was not recommendable because it might cause an increase of liquid membrane viscosity and consequently a decrease of diffusivity and permeability of the complex species.⁵⁰

Another part of the existing research was mostly directed to the exploitation the chemical systems of D2EHPA-mediated LM owing a well-defined transport selectivity towards one or some heavy metal ions for studying configuration and kinetics aspects such as improving the operation and performance of certain LM configurations, testing certain newly developed LM configurations, or for gaining further knowledge about the mass transfer mechanism taking place in the LMs. Thus, these research works led to development of some mathematic models which describe metal ion transport across LMs.⁷⁰ The validity of these models was then verified by fitting theoretical data with experimental ones. The configurations the most studied in the literature were: SLM/strip dispersion configuration,^{39,51} ELMs,⁴⁷ HFSLM,^{44,49}

multimembrane hybrid system (MHS),^{66,67} polymer inclusion membrane (PIM).⁶⁸

The most investigated parameters and their effects on the stability and efficiency of ELMs can be summarized as follows:

- The presence of surfactants (emulsifiers) was necessary for stabilizing emulsion phase, but this reduced the metal transport, particularly at the membrane/receiving phase interface.⁵¹⁻⁵³ So its amount has to be as minimal as possible.

- Main resistance to mass transfer may lie at the outer oil-water interface.⁴³ The parameter of the ratio of organic and intern aqueous phases determines the area of the outer oil-water interface.

- An addition of some surface-active substances, other than surfactants, to the LM phase affects metal ion flux through the membrane; the transport may be accelerated.⁵³

The main influencing parameters and their effects on the stability and efficiency of SLMs can be summarized as follows:

- Although, it was found that, in the large majority of cases, the D2EHPA-mediated LM transport of metal ions were mainly controlled by membrane diffusion, they can be also controlled by both aqueous film and membrane diffusion in some cases⁷¹ when employing simultaneously the following condition: lower metal ion concentration with lower hydrogen ion concentration in feed phase, and higher carrier concentration.

- The use of SLM membrane was limited by a short lifetime of porous solid membranes; where its continuous use was feasible just for several

times. The support membrane needed to be re-impregnated in order to achieve further transport.⁶⁵

In case of D2EHPA-mediated LM systems with BLM being the simplest type and the most stable, the results showed that such configuration tended to cause relatively low fluxes due to its small interfacial area per unit volume,⁵⁹ long transportation path and high membrane resistance. These shortcomings have limited large-scale industrial application for BLMs. The potential applications of existing BLM configurations are restricted to laboratory-scale for studies of transport mechanisms, assessing metal ion transport efficiency and selectivity by D2EHPA systems, and as preconcentration tool for analytic purposes.

From an application point of view, some research works were rather interested in how to use the D2EHPA-mediated LM systems in metal ion separation applications. A possible useful application of these systems is their use in the field of analytic chemistry as preconcentration tool to separate and enrich the heavy metal ion present at very low traces in aqueous samples prior to its determination by an appropriate analytic instrument. The published results in this direction are promising. For example, D2EHPA-mediated LM systems were successfully used for selective separation and concentration of metal ion(s) present at very low traces levels in aqueous samples into receiving phase such as lead,^{45,46} cadmium,⁴² copper ions,⁵⁷ and a mixture of seven heavy metals.⁶³ Compared with the analytical procedures commonly used for trace metal determination in diluted aqueous samples, the new LM systems may be used as a very clean (sample contamination-free), simple, and one-step alternative for semiquantitative, and even quantitative, simultaneous determination of heavy metals in seawater.

For hydrometallurgical applications such as removal and recovery of heavy metal ions from polluted solutions, D2EHPA-mediated LM systems might be applied as novel techniques for mixture component separation from low acidic solutions. For example, Mendiguchia *et al.*⁶³ enabled the simultaneous separation and preconcentration of up to seven heavy metals (copper, zinc, lead, cadmium, aluminum, manganese, and nickel) in seawater, and Singh *et al.*⁶¹ enabled the simultaneous transport of mixture components of copper, nickel and zinc metal ions. But the industrial application of these chemical

systems for treatment of waste water needs to develop existing LM configurations more efficiently and more easiness in operation. In case of BLM configuration, the low efficiency resulting mainly from non-dispersive contact surface could be solved by developing a dispersive BLM configuration like that appeared in one recent study,⁷² where the liquid membrane in closed cycle was passed in the form of multi droplets through both aqueous feed and stripping phases before gathering in its compartment. On the other hand, a configuration called hollow fiber membrane contactors (HFMC) would be more effective membrane unit for ion separation by D2EHPA systems. As a matter of fact, the value of the interfacial area per unit volume can be much higher compared to other LM configurations.⁷³

CONCLUSION

The commercial extractant D2EHPA has extensively coupled with many different LMs in order to separate heavy metal ions from their aqueous solutions. Most of performed research works on this subject are classified following the LM configuration and cation type, then briefly summarized, and reviewed in this paper. These experimental approaches provided further knowledge about the transport of heavy metal ions by D2EHPA-mediated LMs. The overall chemical system selectivities, kinetic behaviors or the feasibility of certain developed LM configurations were intensively studied. It seems that accordingly to the way of selection of the chemical composition conditions, the D2EHPA can be either selective for separation of a single ion from a mixture of other corresponding heavy metal ions or for simultaneous separation of a group of several ions. Practically, some D2EHPA-mediated LMs can be applied in the laboratory as preconcentration tool for heavy metal ion over the detection limits of routine analytical instruments. Further developments or improvements should be performed to the existing LM configurations in order to apply the D2EHPA-mediated LMs on large-scale scale in both hydrometallurgy and the treatment of wastewater for simultaneous removal and recovery of the heavy metal ions. There are still some technical problems such as the slow transport rate in BLMs, operational complexity and emulsion phase breakage in ELMs, and LM phase stability in SLMs.

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